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Selective Metal-to-Ring Alkyl Migration during Irradiation of $CpFe(CO)_2[CHPh(OSiMe_3)]$

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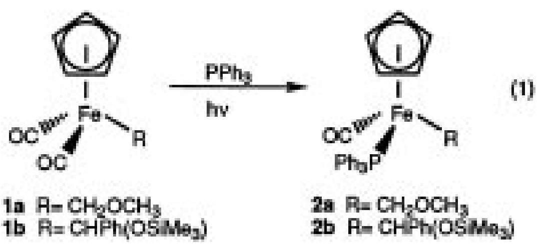
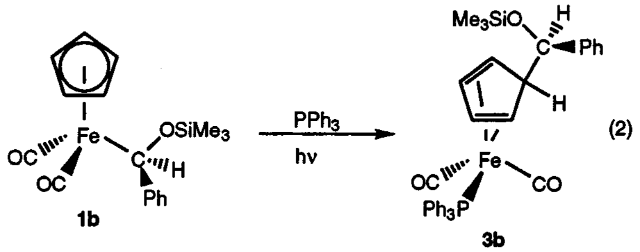
*Summary: UV−vis irradiation of $CpFe(CO)_2[CHPh(OSiMe_3)]$ (**1b**) in the presence of PPh_3 produces η^4-{exo-$C_5H_5[CHPh(OSiMe_3)]$}$Fe(CO)_2PPh_3$ (**3b**), the product of alkyl migration from iron to the Cp ring, in good yield.*

As part of our investigations of carbon-centered organometallic radicals[1] we sought to prepare the iron alkyl complex (η^5-C_5H_5)Fe[CHPh($OSiMe_3$)]$(CO)_2PPh_3$ (**2b**). On the basis of the well-established photosubstitution reactions of $CpFe(CO)_2R$ with PR_3,[2] including the conversion of methoxymethyl complex **1a** to **2a**,[2f] the reaction of siloxyalkyl complex **1b**[3] with PPh_3 appeared to offer a convenient route to **2b** (eq 1). We report here on the unexpected outcome of this reaction.



Irradiation of a 0.2 M benzene/pentane (1:2) solution of **1b** containing 1.1 equiv of PPh_3 (400 W Hg-vapor lamp, Pyrex) for 3.5 h followed by solvent evaporation and chromatography over alumina afforded the yellow solid **3b** as the major product (57%), along with a small amount of $[CpFe(CO)_2]_2$ and an unidentified green compound. Although the FAB mass spectrum of **3b** indicated incorporation of the phosphine (*m/z* 617, M − 1), surprisingly, its IR spectrum exhibited *two* absorptions in the metal carbonyl region (1971, 1911 cm^{-1}) rather than the one expected for **2b**. Furthermore, the ^1H NMR spectrum of **3b** did not show the anticipated single Cp resonance (plus two from the C*H*Ph($OSiMe_3$) and CHPh(OSi*Me*$_3$) groups), but rather, *seven* nonaromatic resonances were present. Similarly, the ^{13}C NMR spectrum of **3b** exhibited five resonances in the 45−85 ppm region, further indicating disruption of the η^5 coordination mode and a lack of molecular symmetry. To establish the structure of **3b** unambiguously, single crystals were obtained from pentane/CH_2Cl_2 and subjected to X-ray diffraction. The resulting molecular structure is shown in Figure 1.



Indeed, the structure of **3b** consists of an $-Fe(CO)_2PPh_3$ fragment coordinated in an η^4 fashion to a cyclopentadiene ligand, substituted with the original alkyl ligand *exo* to the iron fragment. Aside from a disorder associated with the oxygen of the TMS group, no unusual bond distances or angles are observed. The *exo* relationship of the iron and migrated alkyl group strongly suggests a dissociative pathway for the **1b** to **3b** conversion. The stereocenter of the −CHPh($OSiMe_3$) group renders the β- and γ-pairs of cyclopentadienyl carbons (and hydrogens) inequivalent (diastereotopic), accounting for the unsymmetrical NMR spectra of **3b**.

The **1b** to **3b** conversion, though unusual, is not without precedent. Although ligand substitution is the dominant pathway in photoreactions of $(C_5R_5)M(CO)_2R'$ complexes, iron-to-Cp migration of alkyl groups has been observed.[2g] The substitution quantum yield has been found to be much higher than that for metal−carbon bond homolysis, but migration to form (η^4-cyclopentadiene)$Fe(CO)_3$ complexes can become significant under CO pressure, since the net CO substitution is suppressed.[2g] The present result, in which migration greatly predominates over substitution even under nitrogen, is extraordinary when contrasted with the exclusive photosubstitution observed for the electronically similar complex **1a** (→ **2a**).[2f] The *exo* relationship of the migrated alkyl group relative to iron in **3b** is strongly suggestive of a dissociative migration pathway.

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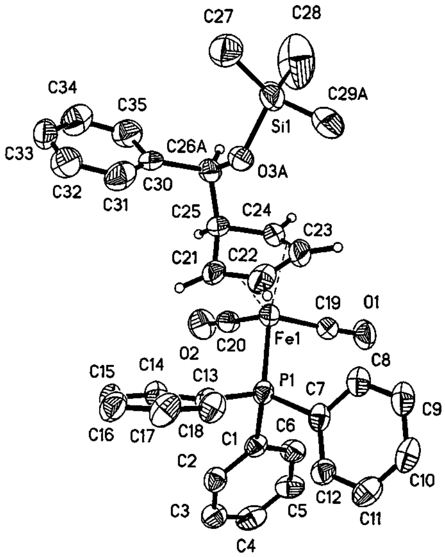

Figure 1. ORTEP diagram for **3b** (50% thermal ellipsoids). Selected bond lengths (Å) and angles (deg): Fe1−C20, 1.764(6); Fe1−C19, 1.776(5); Fe1−C22, 2.044(6); Fe1−C23, 2.045(6); Fe1−C24, 2.099(6); Fe1−C21, 2.114(5); Fe1−P1, 2.215(2); C21−C22, 1.414(7); C21−C25, 1.508(8); C22−C23, 1.410(9); C23−C24, 1.407(9); C24−C25, 1.517(7); C25−C26A, 1.51(2); C20−Fe1−C19, 102.2(2); C20−Fe1−P1, 100.6(2); C19−Fe1−P1, 93.1(2); O1−C19−Fe1, 177.1(5); O2−C20−Fe1, 177.9(5); C22−C21−C25, 109.7(5); C23−C22−C21, 105.9(6); C24−C23−C22, 107.0(5); C21−C25−C24, 93.8(4); O3A−C26A−C25, 105.6(11).

The efficiency of this reaction in the nonpolar medium and the formation of $[CpFe(CO)_2]_2$ is most consistent with Fe−C homolysis. The dominance of the metal-to-Cp pathway in the conversion of **1b** to **3b** (*vis à vis* **1a** → **2a**) may be the combined result of the weaker benzylic metal bond in **1b**[4] and the instability of the alternative, sterically crowded substitution product, **2b**.

Experimental Section

General Considerations. All reactions and manipulations involving organometallic compounds were conducted under an atmosphere of prepurified nitrogen using standard Schlenk line techniques. Reagent grade tetrahydrofuran, diethyl ether, hexane, and benzene were distilled under nitrogen from sodium benzopheneone ketyl; dichloromethane was dried by distillation from CaH_2. All reagents were obtained commercially and used without further purification. The complex $(\eta^5\text{-}C_5H_5)Fe[CHPh(OSiMe_3)](CO)_2$ (**1b**) was prepared as described by Hossain.[3]

Photoreaction of $(\eta^5\text{-}C_5H_5)Fe[CHPh(OSiMe_3)](CO)_2$ (1b) with PPh_3. A solution of **1b** (0.25 g, 0.70 mmol) and PPh_3 (0.19 g, 0.74 mmol) dissolved in a mixture of 1 mL of benzene and 2 mL of pentane was placed in a Schlenk tube under nitrogen. The vessel was mounted next to a 400 W Hanovia (Hg vapor) jacketed lamp, the entire assembly was cooled to 0 °C, and the reaction mixture was then irradiated for 3 h. The mixture was then added to the top of an activity III (neutral) alumina column under nitrogen. Elution with 5/95 ether/petroleum ether afforded a small amount of unreacted **1b** followed by an orange band which, when concentrated, afforded **3b** (0.17 g, 57%) as a golden foam: IR ($CHCl_3$) 1971, 1911 cm^{-1}; ^1H NMR (C_6D_6) δ 7.2−7.9 (m, 20H), 5.20 (s, 1H), 5.10 (s, 1H), 3.61 (d, J = 8, 1H), 3.45 (d, J = 8, 1H), 2.88 (s, 1H), 2.46 (s, 1H), 0.10 (s, 9H); ^{13}C NMR (C_6D_6) δ 220.1 (d, J = 12), 219.2 (d, J = 15), 136.8, 136.4, 133.2 (d, J = 10), 132.4 (d, J = 10), 131.6, 129.7, 127.0, 126.6, 83.2 (d, J = 6), 83.0 (d, J = 8), 64.7, 54.7, 50.3, 0.3; MS (FAB, NBA) m/z 617 (10, M − 1), 439 (100, M − $CHPhOSiMe_3$). Elution with 20/80 ether/petroleum ether produced a dark red band of $[CpFe(CO)_2]_2$ and a green band which was not characterized.

Table 1. Crystal Data and Structure Refinement Details for 3b

empirical formula	$C_{35}H_{35}FeO_3PSi$
fw	618.54
temp	173(2) K
wavelength	0.710 73 Å
cryst syst	triclinic
space group	$P\bar{1}$
unit cell dimens	a = 10.6768(14) Å
	b = 13.001(2) Å
	c = 13.147(2) Å
	α = 100.037(8)°
	β = 105.714(9)°
	γ = 110.954(8)°
volume, Z	1564.1(4) Å^3, 2
density (calcd)	1.313 g/cm^3
abs coeff	0.605 mm^{-1}
F(000)	648
cryst size	0.32 × 0.42 × 0.36 mm
θ range for data collecn	1.76−25.00°
no. of rflns collected	5596
no. of indep rflns	5249 (R(int) = 0.0780)
max and min transmissn	0.7370 and 0.4945
no. of data/restraints/params	5243/0/401
goodness of fit on F^2	1.048
final R indices ($I > 2\sigma(I)$)	R1 = 0.0602, wR2 = 0.1251
R indices (all data)	R1 = 0.1147, wR2 = 0.1728

X-ray Structure Determination. Crystals of **3b** were obtained from hexane/CH_2Cl_2 at −10 °C. X-ray data were collected at −100 °C on a Siemens P-4 diffractometer using Mo Kα (λ = 0.710 69 Å) radiation. The data were corrected for Lorentz and polarization effects; an empirical absorption correction based on ψ scans was applied. The structure was solved by the direct method using SHELXTL 5.0 and refined by full-matrix least squares on F^2 using all reflections. Hydrogen atoms were included in the refinement with idealized parameters.The final R1 = 0.60 is based on 3291 observed reflections ($I > 2\sigma(I)$). Hydrogen atoms, except H21, H22, H23, H24, and H26A, are omitted in Figure 1 for clarity. Details of the crystal data and refinement are given in Table 1.

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Supporting Information Available: Tables of atomic coordinates and isotropic displacement factors, bond lengths and angles, anisotropic displacement factors, hydrogen coordinates, selected torsion angles, and least-squares planes and deviations from them and an additional figure giving the structure for **3b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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